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Utilization of thermodesorption coupled to GC–MS to study stability of different wood species to thermodegradation

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ABSTRACT

Thermodesorption coupled to gas chromatography coupled to mass spectroscopy (TD-GC–MS) has been investigated to identify volatile degradation products generated during wood heat treatment by mild pyrolysis. For this purpose, wood samples of different softwood and hardwood species have been heat treated under nitrogen for different temperatures comprised between 180 and 230 °C during 15 min in the glass thermal desorption tube of the thermodesorber and the volatile wood degradation products trapped. The trapped products were then thermodesorbed and analysed by GC–MS. Chromatograms of the different samples indicated the formation of different products resulting from degradation of lignin and hemicelluloses. Hardwoods were shown to be more sensitive to thermodegradation than softwoods, for which degradation products appear at slightly higher temperature. The important formation of acetic acid is concomitant with the formation of most of degradation products and at the origin of the difference of reactivity observed between softwoods and hardwoods.

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1. Introduction

Utilization of wood as building material is subjected to increasing interest due to its intrinsic properties and its ability to fix carbon dioxide. However, in spite of numerous advantages like its cost, availability, workability, thermal performance and aesthetics, wood is susceptible to deterioration by micro-organisms under specific adverse conditions justifying the use of adequate preservation treatment. Wood heat treatment has been reported as an attractive alternative preservation method to classical methods based on utilization of biocides, which enables the treated wood to remain an environmentally friendly product. Wood heat treatment induces chemical modifications of cell wall components responsible of the improvement of wood properties. Lignin polymer network is modified [1,2], crystallinity of cellulose is modified [3,4], hemicelluloses are strongly degraded [3,5,6]. Chemical reactions involved during wood heat treatment as well as the final properties of the material depend directly on the treatment temperature and duration. Recently, it was also reported that mass loss caused by thermodegradation reactions and resulting wood elemental composition could be a reliable and accurate marker to predict decay resistance of heat-treated wood [7–11]. Indeed, previous studies have shown that heat treatment involves numerous dehydration reactions of amorphous polysaccharides [2–4,12] leading to formation of volatile by-products like furfural or hydroxymethylfurfural and to the formation of carbonaceous materials within the wood structure at the origin of the strong decrease of wood's O/C ratio [6,13]. In the same time, depolymerization of lignin network through cleavage of α or β-arylether linkage or dehydration reactions lead to the formation of numerous low molecular weight phenolic compounds [14–16]. Identification and quantification of volatile degradation products is of important to have better insight on mechanisms of wood thermodegradation to understand the different kinetics of degradation observed between softwoods and hardwoods. Such results are of great interest to improve industrial heat treatment processes and to be able to develop numerical methods to predict final properties of the material. Previous study showed that kinetic of degradation for similar curing conditions are strongly influenced by the nature of the wood species used [11]. During this study, softwoods (pine and Silver fir) have been shown to be more resistant to thermodegradation than hardwoods (beech, poplar and ash) as demonstrated by the lower weight losses recorded for boards treated using conductive heat treatment under nitrogen. Even if wood density cannot be totally excluded to explain these differences, wood species of lower densities being generally more resistant to thermodegradation than those of higher densities, wood chemical composition should also be involved to explain observed. differences. Higher susceptibility of hardwoods has been attributed to their hemicelluloses composition. Indeed, softwoods contain galactoglucomannan

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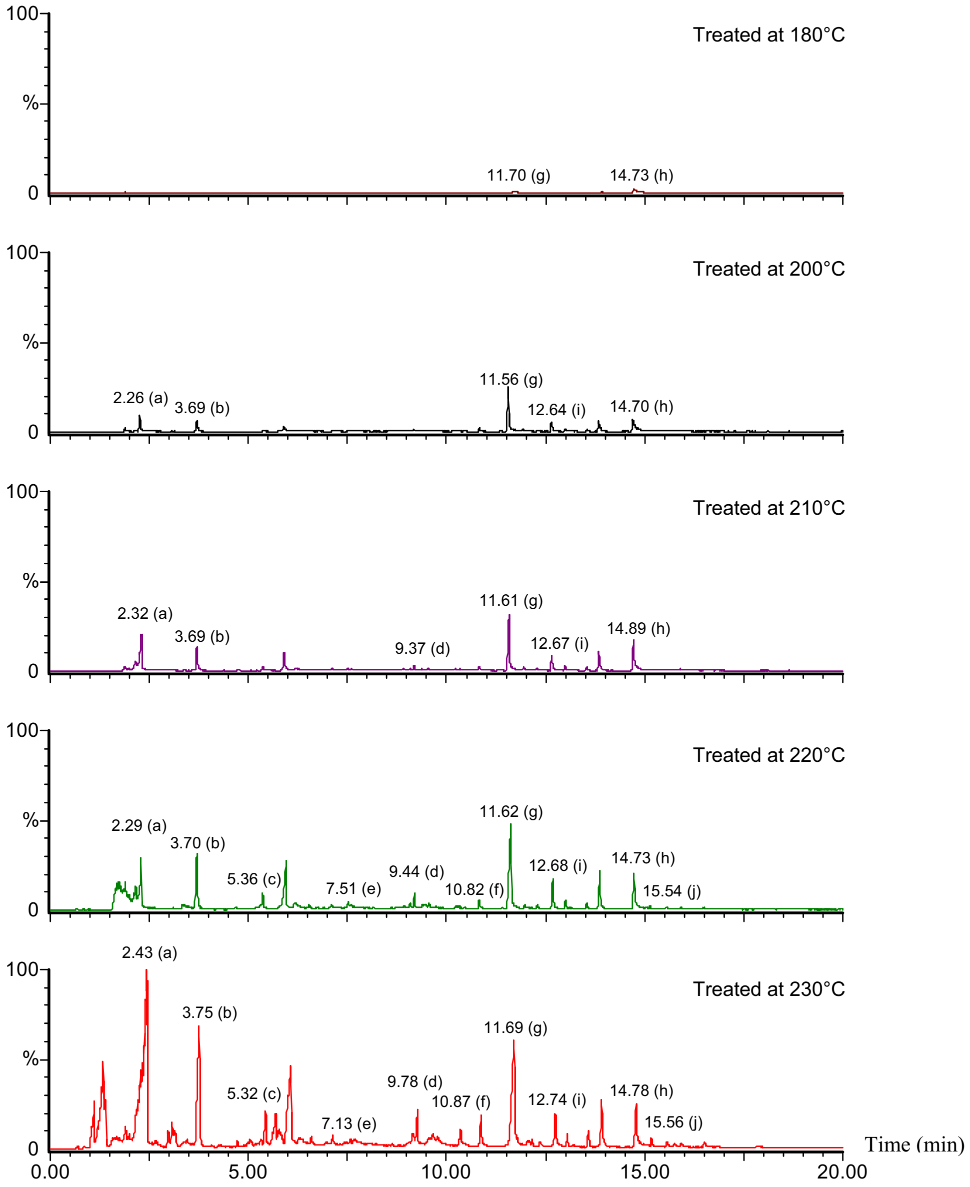

Fig. 1. Degradation products identified by TD-GC–MS from beech sawdust heat treated under helium during 15 min at different temperatures.

and arabinoglucuronoxylan, while hardwoods contain mainly glucuronoxylan and low amount of glucomannan. Moreover, xylan units of hardwood glucuronoxylan are strongly acetylated, comparatively to softwood hemicelluloses for which acetyl groups are attached to the glucomannan backbone [12,17]. Deacetylation of hemicelluloses causes liberation of acetic acid, which catalyzes depolymerization of the less ordered carbohydrates like hemicelluloses and amorphous cellulose. Similar results have been described by Prins and co-workers during torrefaction of woody biomass carried out at slightly higher temperatures ranging from 230 to 300 °C [18]. Deciduous wood types (beech and willow) were found to produce more volatiles than coniferous wood (larch) constituted especially of acetic acid and methanol. These authors attributed this difference of reactivity to the acetoxy and methoxy groups present as side chains in xylose units present in the xylan containing hemicellulose fraction.

The aim of this study is to give better insights on wood thermodegradation pathways during wood heat treatment by mild pyrolysis with special emphasis on the effects of the nature of the wood species and of the treatment temperature on the generation of volatile by-products. For this purpose, two softwoods and three hardwoods species were investigated and analysed using thermodesorption coupled to gas chromatography coupled to mass spectroscopy. Treatment was performed directly in the glass thermal desorption tube of the thermodesorber at temperatures ranging from 180 °C to 230 °C allowing easy analysis of all volatile by-products formed during thermal treatment.

2. Experimental

2.1. Material

Two different softwood (pine, *Pinus sylvestris* L. and Silver fir, *Abies pectinata* Lam) and three different hardwood species (beech, *Fagus sylvatica* L.; poplar, *Populus nigra* L.; ash, *Fraxinus excelsior* L.) were used during this study. Wood was grounded to fine sawdust and passed through different sieves to obtain a powder of granulometry comprised between 0.2 and 0.5 mm. Sawdust was

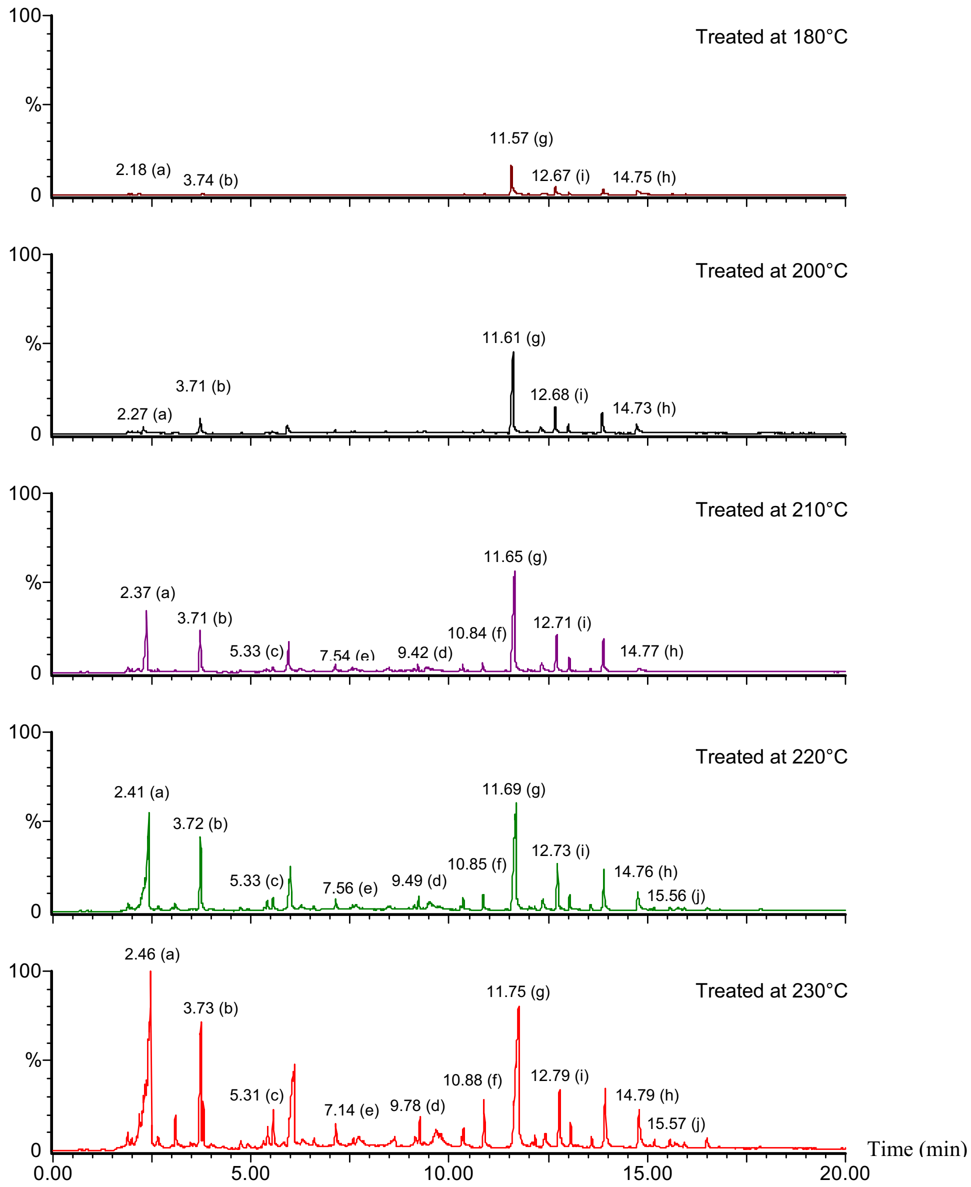

Fig. 2. Degradation products identified by TD-GC–MS from poplar sawdust heat treated under helium during 15 min at different temperatures.

conditioned at 103 °C for 24 h and stored in closed bottle before analysis.

2.2. *Thermodesorption-GC–MS*

Thermodesorption, coupled to GC/MS, permits analysis of volatile and semi volatile organics directly from small sample sizes without the need for solvent extraction or other steps of sample preparation reducing the risks to loss products. Thermodesorption phase is divided in two steps: a first step concerning heat treatment under inert atmosphere during which volatile and semi volatile products resulting from wood polymer degradation are formed and trapped on Tenax, and a second step during which these products are desorbed at 300 °C and transferred to the column for GC–MS analysis. The typical procedure used during our experiment is described thereafter. Approximatively 30 mg of sawdust of the different wood species were placed in the glass thermal desorption tube (O.D. ¼ in. × *L* 3½ in., Supelco) and centred between two pieces of glass wool. Thermal treatment was performed in a Turbomatrix 300 Thermal Desorber system (Perkin Elmer, USA) allowing thermal treatments in the range of 50–400 °C during different times. The conditions were: pre-purge for 1 min at room temperature using helium carrier gas at 1 mL min^{-1}, heating at the required temperature for 15 min using carrier gas at 20 mL min^{-1} and splitless trapping at −30 °C. The trap was then desorbed at 300 °C for 1 min at 1 mL min^{-1} through a transfer line at 300 °C with a split flow of 40 mL min^{-1}. Quantification of degradation products was expressed in peak absolute surface unit per mg of sawdust used for TD-GC–MS analysis. Maximum relative standard deviation calculated from 3 replicates for given curing conditions was estimated to ±5%.

3. Results and discussion

To check the effect of the nature of the wood species and obtain better insights in the mechanisms of thermodegradation, TD-GC–MS analyses have been performed on the different wood species. For this purpose, a few mg of sawdust placed in the thermodesorption tube of the thermodesorber were heated under nitrogen during 15 min at different temperatures ranging from

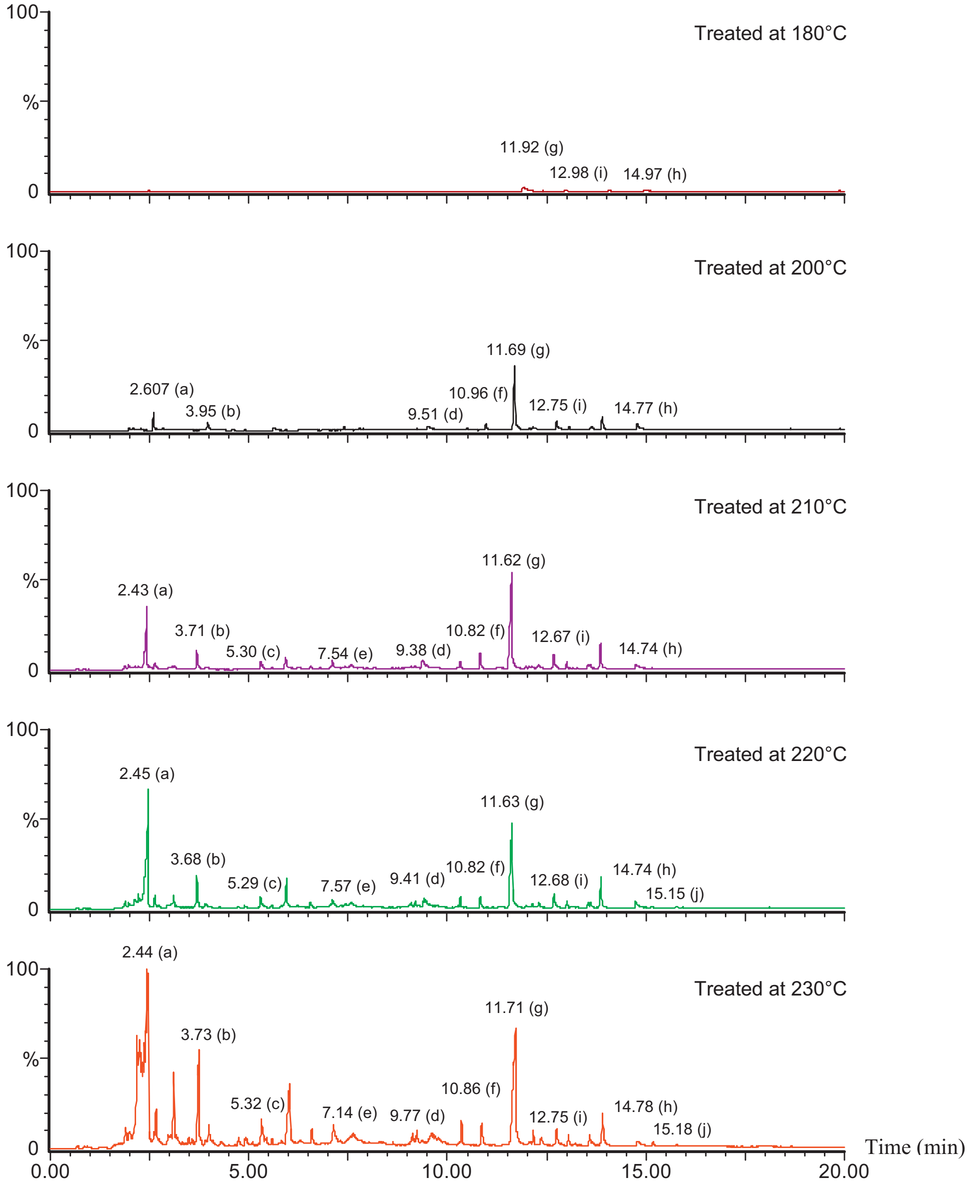

Fig. 3. Degradation products identified by TD-GC–MS from ash sawdust heat treated under helium during 15 min at different temperatures.

180 °C to 230 °C. Degradation products formed during heating were trapped on adsorbent before thermodesorption at 300 °C and GC–MS analysis. The chromatograms of the degradation products formed at the different temperatures for the different wood species are presented in Figs. 1–5

As observed during our previous studies, behaviour of hardwood and softwood species is quite different. Except small amounts of acetic acid at 2.45 min, vanillin at 11.5 min, acetovanillone at 12.7 min and an unidentified product at 13.85 min, no degradation products were detected for both softwood species up to 210 °C. Heating at higher temperatures resulted in a progressive apparition of higher quantities of acetic acid, furfural at 3.7 min, methylfurfural at 5.3 min and hydroxymethylfurfural at 9.4 min resulting from hemicelluloses degradation. Formation of these products is concomitant to acetic acid apparition corroborating its role in hemicelluloses degradation mechanisms [19]. Formation of acetic acid appears at lower temperature in the case of hardwoods resulting in a more rapid degradation of hemicelluloses comparatively to softwoods. At the same time, different lignin degradation products like guaiacol at 7.1 min, syringol at 10.8 min, eugenol at 12.0 min, methoxyeugenol at 15.1 min or *p*-vinylguaiacol at 10.35 min appear. Syringaldehyde was also detected in all hardwood degradation products in addition to vanillin resulting from guaiacyl and syringyl units respectively. Formation of these products may be explained on the basis of numerous degradation reactions involving different reactional mechanisms. Fig. 6 describes some possible reactional pathways based on a simple lignin model. It is probable that lignin degradation mechanisms involve both heterolytic and homolytic or free radical mechanisms. These latter ones are supported by the strong increase of free radical species observed by ESR after wood thermal treatment [20]. Most of these radical species have been attributed to phenoxyl radicals formed either on wood macromolecules or on extractives. Stability of phenoxyl and benzylic radicals formed may explain in great part these homolytic cleavage reactions. Degradation of amorphous polysaccharides occurred simultaneously to the formation of acetic acid, which has been reported to catalyze dehydration reactions to anhydrosugars [19]. Depolymerization of hemicelluloses leads to the formation of pentoses like xylose and arabinose and hexoses like mannose, glucose and galactose at

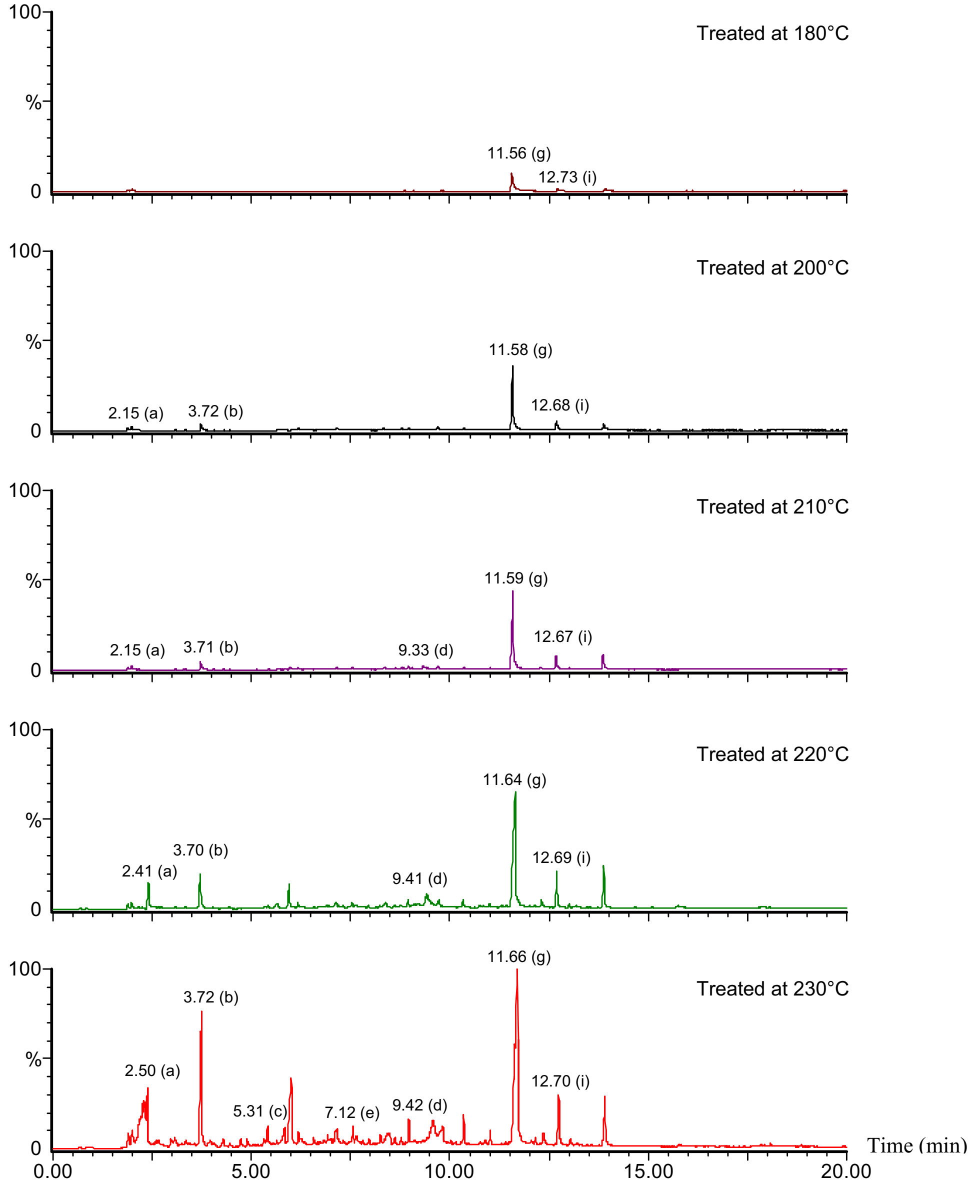

Fig. 4. Degradation products identified by TD-GC–MS from pine sawdust heat treated under helium during 15 min at different temperatures.

the origin of the formation of furfural and hydroxymethylfurfural through dehydration reaction respectively. These observations are consistent with those of Simkovic et al., who used TG/MS to study thermal decomposition of xylan and observed high amounts of acetic acid and water as the main liquid torrefaction products [21]. Formation of methylfurfural is probably due to homolytic breakdone of the C–O bond resulting in the formation of a stable radical in α position of the furan ring. In addition to the different degradation products mentioned above, numerous low molecular weight ketones, aldehydes, lactones and acids similar to those formed during wood toasting [22] are formed in more or less important quantities during thermal treatment of the different wood species.

To be able to quantify more precisely the difference of susceptibility to thermodegradation of the wood species studied, peaks of the main degradation were integrated. Each peak has been integrated from the total ion current and expressed in surface unit per mg of sawdust used for TD-GC–MS analysis. To facilitate comparisons, each peak has then been normalized on the basis of the peak of acetic acid formed during beech heat treatment at 230 °C, which present the highest intensity and for which an arbitrary value of 100 has been attributed. Tables 1 and 2 show the relative intensities of the main degradation products formed as a function of treatment temperature.

It is obvious from Table 1 that production of acetic acid is much more important in the case of hardwoods than in the case of softwoods. At 230 °C, up to ten times more acetic acid is produced in the case of beech comparatively to pine and Silver fir, while its production is six to seven times more important in the case of poplar and ash, respectively.

Formation of furfural is more important in the case of hardwoods comparatively to softwoods traducing the higher susceptibility to degradation of pentoses present in hardwoods hemicelluloses [23]. Formation of hydroxymethylfurfural and methylfurfural is less important compared to furfural and occur in a more or less similar way independently of the nature of the wood species.

For all wood species, vanillin is the most abundant phenolic degradation product formed during heat treatment. This product

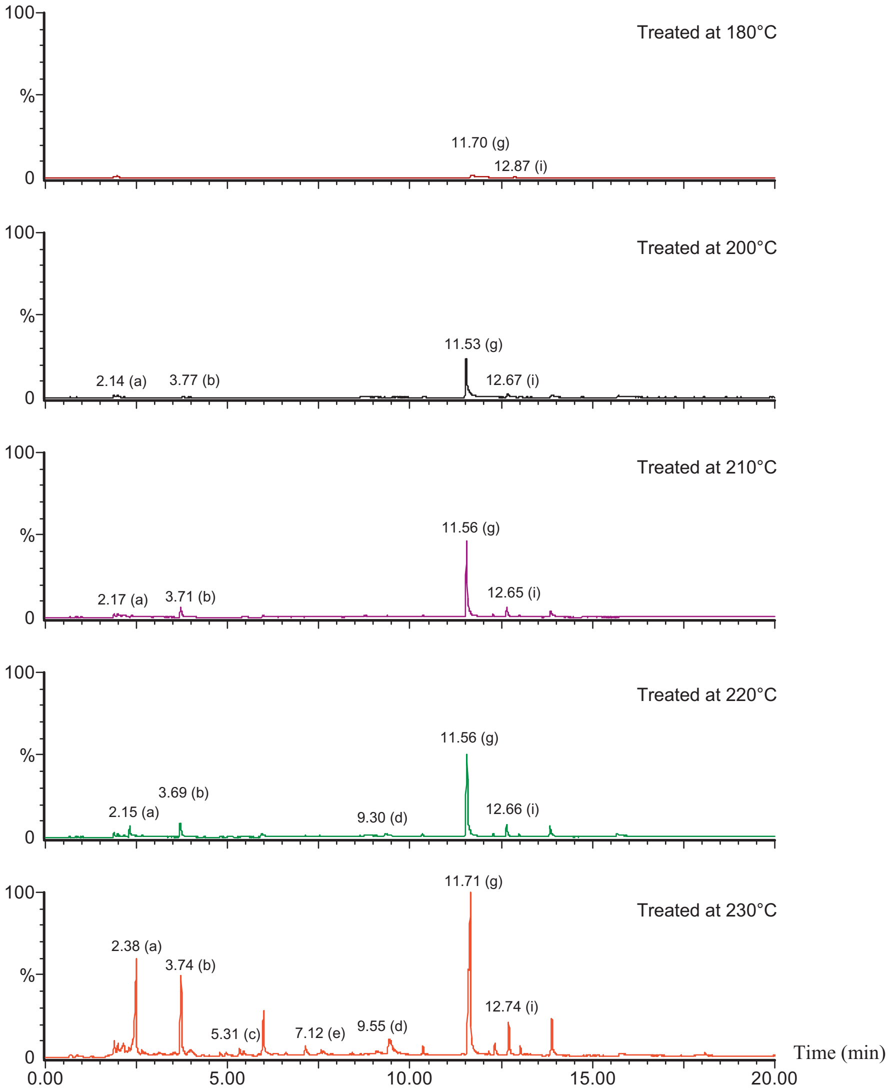

Fig. 5. Degradation products identified by TD-GC–MS from Silver fir sawdust heat treated under helium during 15 min at different temperatures.

Table 1
Evolution of the relative intensities[a] of the main hemicelluloses degradation products.

Product	Retention time (min)[b]	Wood species	Treatment temperature (°C)				
			180	200	210	220	230
Acetic acid	2.50	Pine	0.0	0.1	0.1	0.2	9.7
	2.38	Silver fir	0.0	0.0	0.7	3.6	12.8
	2.43	Beech	0.0	3.0	11.9	38.7	100.0
	2.46	Poplar	0.0	2.7	9.6	29.1	61.8
	2.44	Ash	0.0	2.1	6.5	20.5	68.5
Furfural	3.72	Pine	0.0	0.0	1.2	2.0	4.7
	3.74	Silver fir	0.0	0.7	1.0	4.0	10.9
	3.75	Beech	0.0	1.9	5.0	8.1	26.2
	3.73	Poplar	0.0	2.4	5.7	11.2	17.9
	3.73	Ash	0.0	1.1	0.1	3.7	8.3
Methylfurfural	5.31	Pine	0.0	0.0	0.1	0.3	0.4
	5.31	Silver fir	0.0	0.0	0.0	0.0	0.4
	5.32	Beech	0.0	0.0	0.0	0.0	0.6
	5.31	Poplar	0.0	0.1	0.3	0.5	0.4
	5.32	Ash	0.0	0.0	1.1	1.5	2.7
Hydroxymethylfurfural	9.42	Pine	0.0	0.0	0.4	1.1	2.6
	9.55	Silver fir	0.0	0.0	0.5	3.4	4.7
	9.78	Beech	0.0	0.0	0.9	1.2	4.1
	9.78	Poplar	0.0	0.5	1.4	3.6	8.6
	9.77	Ash	0.0	0.1	0.2	2.3	3.9

[a] Maximum relative standard deviation = 5%.

[b] Retention time at 230 °C.

Table 2
Evolution of the relative intensities[a] of the main lignin degradation products.

Product	Retention time (min)[b]	Wood species	Treatment temperature (°C)				
			180	200	210	220	230
Acetic acid	2.50	Pine	0.0	0.1	0.1	0.2	9.7
	2.38	Silver fir	0.0	0.0	0.7	3.6	12.8
	2.43	Beech	0.0	3.0	11.9	38.7	100.0
	2.46	Poplar	0.0	2.7	9.6	29.1	61.8
	2.44	Ash	0.0	2.1	6.5	20.5	68.5
Guaiacol	7.12	Pine	0.0	0.0	0.0	0.0	0.7
	7.12	Silver fir	0.0	0.4	0.0	0.0	0.8
	7.13	Beech	0.0	0.2	0.4	0.4	1.0
	7.14	Poplar	0.0	0.4	0.8	1.4	2.4
	7.14	Ash	0.0	0.1	1.1	2.0	2.9
Syringol	–	Pine	0.0	0.0	0.0	0.0	0.0
	–	Silver fir	0.0	0.0	0.0	0.0	0.0
	10.87	Beech	0.0	0.4	1.8	1.1	3.7
	10.88	Poplar	0.0	0.6	1.0	2.1	5.5
	10.86	Ash	0.0	0.2	1.6	1.2	2.5
Vanillin	11.66	Pine	0.0	6.7	9.5	12.9	15.4
	11.71	Silver fir	0.0	8.1	9.5	21.1	26.9
	11.69	Beech	0.0	7.5	14.7	17.6	23.6
	11.75	Poplar	0.1	15.7	20.8	26.5	36.6
	11.71	Ash	0.0	0.6	13.6	14.6	20.6
Syringaldehyde	–	Pine	0.0	0.0	0.0	0.0	0.0
	–	Silver fir	0.0	0.0	0.0	0.0	0.0
	14.78	Beech	0.0	3.9	–	6.1	6.2
	14.79	Poplar	0.0	2.8	1.4	3.7	6.1
	14.78	Ash	0.0	0.0	1.5	1.6	1.3
Acetovanillin	12.70	Pine	0.0	1.3	2.1	3.1	4.0
	12.74	Silver fir	0.0	2.5	3.4	8.1	7.4
	12.74	Beech	0.0	3.5	8.2	8.9	10.7
	12.79	Poplar	0.0	7.3	9.1	12.8	16.8
	12.75	Ash	0.0	0.0	4.3	5.1	2.0
Acetosyringon	–	Pine	0.0	0.0	0.0	0.0	0.0
	–	Silver fir	0.0	0.0	0.0	0.0	0.0
	15.56	Beech	0.0	0.1	18.0	0.4	1.3
	15.57	Poplar	0.0	0.0	0.0	0.5	0.0
	–	Ash	0.0	0.0	0.0	0.0	0.0

[a] Maximum relative standard deviation = 5%.
[b] Retention time at 230 °C.

is generally present in small quantities in all the wood samples even at 180 °C. Syringaldehyde is formed during thermal treatment of hardwoods species for temperatures higher or equal to 210 °C. Acetovanillin is the second more abundant phenolic degradation product. Its formation starts at 200 °C and increases progressively with the increase of treatment temperature. Similarly to syringaldehyde, formation of acetosyringon is less obvious. Guaiacol and syringol are formed at higher temperatures and their concentrations remain relatively low compared to previous lignin degradation products.

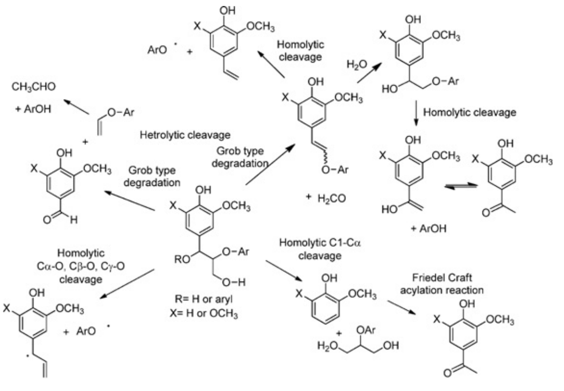

Fig. 6. Some possible pathways involved in lignin degradation under mild pyrolysis.

4. Conclusion

TD-GC–MS appears as an attractive tool to study volatile products formed during wood thermodegradation. Softwoods investigated during this study (pine, Silver fir) are less sensitive to thermodegradation than hardwoods (beech, ash, poplar). High amounts of acetic acid generated during thermodegradation of strongly acetylated glucuronoxylan of hardwoods is associated to the formation of numerous degradation product resulting from lignin as well as hemicelluloses acid catalyzed degradations. Taking into account the intrinsic differences between softwoods and hardwoods based on their different chemical compositions, the main degradation products identified are relatively similar except as concerns degradation products resulting from guaiacyl and syringyl units. The main difference concerns the kinetic of thermodegradation, which is directly influenced by treatment temperature and quantity of acetic acid liberated during thermal treatment. The degree of acetyl group present initially in wood could be therefore an important parameter to determine curing conditions to obtain a given level of thermodegradation. Results obtained clearly indicated that thermal degradation of lignin and hemicelluloses begin in a range of temperatures comprised between 210 and 230 °C, degradation of hardwoods beginning at slightly lower temperatures comparatively to softwoods. Further studies are currently under investigation using reference compounds to identify more precisely the origins of the different thermodegradation products. Knowledge of the thermodegradation pathways during wood heat treatment could enable more accurate determination of the curing conditions (time and temperature) according to the nature of the wood species allowing thus to improve heat treatment processes and consequently properties of the heat treated products.

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